

Structure – Oxygen Reduction Reaction Activity Relationships in Porous Hollow PtNi/C Nanoparticles

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Abstract

Enhancing the specific activity and the mass activity of oxygen reduction reaction (ORR) catalysts in proton-exchange membrane fuel cells is currently achieved by alloying Pt with an early or late transition metal. Using hollow PtNi/C nanoparticles with different physico-chemical properties (Ni content, lattice parameter, specific surface area), we show that structural defects such as grain boundaries also contribute to the catalytic enhancement for the ORR. To quantify their concentration, we used the structure sensitivity of the CO_{ads} monolayer electrooxidation reaction, namely the presence

of an oxidation pre-peak in CO_{ads} stripping voltammograms. A straightforward relationship was established between the ratio of the charge under the pre-peak ($Q_{pp, CO}$) to the total CO_{ads} electrooxidation charge and the specific activity for the ORR. The present study provides a knowledge base for designing more efficient ORR electrocatalysts.

Key Words: Proton Exchange Membrane Fuel Cells; Oxygen Reduction Reaction; Hollow PtNi/C Electrocatalysts; Structural Defects; Grain Boundaries.

Introduction

The electrocatalytic properties of a metal or an alloy strongly depend on local atomic features such as the chemical composition, the crystallographic orientation of the facets, the type/density of structural defects, and the average coordination number of the atoms. A very important case is that of Pt alloys used to electrocatalyze the oxygen reduction reaction (ORR) in proton-exchange membrane fuel cells (PEMFCs). The interest for Pt alloys stems from studies published in the late 1980s-1990s, which showed that the presence of a 3d transition metal modifies the local electronic structure of Pt, and thus its catalytic activity for the ORR. This effect was later rationalized within the frame of the *d*-band theory developed by Hammer and Nørskov ^[1,2]. The authors showed that the interactions between the metal surface and a given adsorbate depend on the *d*-band centre (ϵ_d) and of its degree of filling. An important corollary is that the *d*-band centre determines the chemisorption energy of several adsorbates. In the last decade, the theory developed by Hammer and Nørskov has become the cornerstone for the development of 'catalysts-by-design', *i.e.* ORR electrocatalysts specifically tailored to decrease the chemisorption energy of the reaction intermediates (OOH_{ads}, O_{ads}

and OH_{ads}) [3–10]. Relevant examples of such 'catalysts-by-design' include but are not limited to 'Pt-monolayer catalysts' by Adzic's group [11], 'Pt-skin' and 'Pt-skeleton' electrocatalysts from Stamenkovic's group, [4,12] core@shell and dealloyed electrocatalysts from Strasser's group [9,13].

The ORR is also a highly structure sensitive reaction as shown by the 90-fold increase of the ORR specific activity at $E = 0.90$ V vs. the reversible hydrogen electrode (RHE) reported by Stamenkovic *et al.* [3] on a Pt_3Ni (111) single crystal relative to a commercial Pt/C [the catalytic improvement was 10-fold vs. Pt (111)]. This study paved the way to the synthesis of preferentially-shaped bimetallic ORR electrocatalysts, which combine the positive effects of strain, ligand, and structure sensitivity on ORR kinetics. Cui *et al.* [14] first synthesized $\text{Pt}_x\text{Ni}_{1-x}$ nano-octahedra with three different atomic compositions ($\text{Pt}_{60}\text{Ni}_{40}$, PtNi and $\text{Pt}_{40}\text{Ni}_{60}$). However, Ni atoms preferentially segregate at the (111) facets in nano-octahedra, thereby facilitating their dissolution upon exposure to acidic electrolyte, and resulting in a severe decrease of the long-term ORR activity. Doping $\text{Pt}_x\text{Ni}_{1-x}$ with rhodium (Rh) atoms recently proved beneficial to stabilize the octahedral structures but could not prevent a dramatic decrease of the ORR activity during potential cycling (70 % of the initial specific activity at $E = 0.90$ V vs. RHE was lost after 30,000 potential cycles between 0.05 and 1.00 V vs. RHE) [15]. Using galvanic replacement and Kirkendall effect (a vacancy-mediated interdiffusion mechanism observed in bi-metallic materials driven by the faster diffusion of one metal with respect to the other [16,17]), Chen *et al.* [18] recently prepared Pt_3Ni nanoframes with porous architecture by eroding Ni atoms from PtNi_3 polyhedra. The authors reported a 16-fold enhancement in ORR specific activity at $E = 0.95$ V vs. RHE on $\text{Pt}_3\text{Ni}/\text{C}$ nanoframes vs. Pt/C [18], and claimed constant catalytic activity during 10,000 potential cycles between 0.60 and

1.00 V vs. RHE (liquid electrolyte, $T = 298$ K). It has also been shown that porous nanostructures form spontaneously from bimetallic alloys during model ^[19–21] or real PEMFC operating conditions ^[22–26]; therefore, they can be considered as the stable nanostructure after dissolution of the alloying element (which is usually less noble than Pt e.g. Co, Ni, Cu). A combination of Kirkendall effect and galvanic replacement was recently used by Dubau *et al.* ^[25,27–29] to synthesize porous hollow PtCo/C or PtNi/C nanoparticles, composed of a hollow core surrounded by a PtNi shell. The authors reported a 9-fold enhancement in ORR specific activity and a 6-fold enhancement in ORR mass activity at $E = 0.95$ V vs. RHE compared to a commercial Pt/C, respectively. In addition, the hollow PtNi/C nanostructures exhibited remarkable durability as evidenced by the results obtained in real ^[24–26] or model ^[28] PEMFC operating conditions.

Herein, in an effort to rationalize the enhanced ORR activity of this class of nanomaterials, we synthesized a set of porous hollow PtNi/C nanostructures featuring different Ni content, Pt lattice contraction, and fraction of structural defects (estimated using CO as a molecular probe ^[30–32]). A direct relationship was found between the ratio of the charge under the pre-peak ($Q_{pp, CO}$) to the total CO_{ads} electrooxidation charge ($Q_{T, CO}$) and the specific activity for the ORR on hollow PtNi/C nanostructures, which is discussed at the light of the structure sensitivity of these electrochemical reactions.

Results and Discussion

Figure 1 displays transmission electron microscopy (TEM) images of hollow PtNi/C nanoparticles synthesized at room temperature (*i.e.* without temperature control, $T = 298 \pm 5$ K) by a one-pot surfactant-free method first described by Bae *et al.* ^[33]. As it proved to be optimal in terms of ORR activity, ^[28] a (Pt:Ni) ratio of 1:3 was used in the

initial metal salt precursor solution. The exact growth mechanism of hollow nanostructures remains poorly understood to date. However, Ni/C or Ni-B/C nanoparticles are believed to form first, and then oxidize into Ni^{2+} ions (loss of electrons) upon contact with the Pt^{2+} ions in solution [the driving force comes from the difference in standard potential between the Pt^{2+}/Pt and Ni^{2+}/Ni redox couples (galvanic replacement) ^[34]].

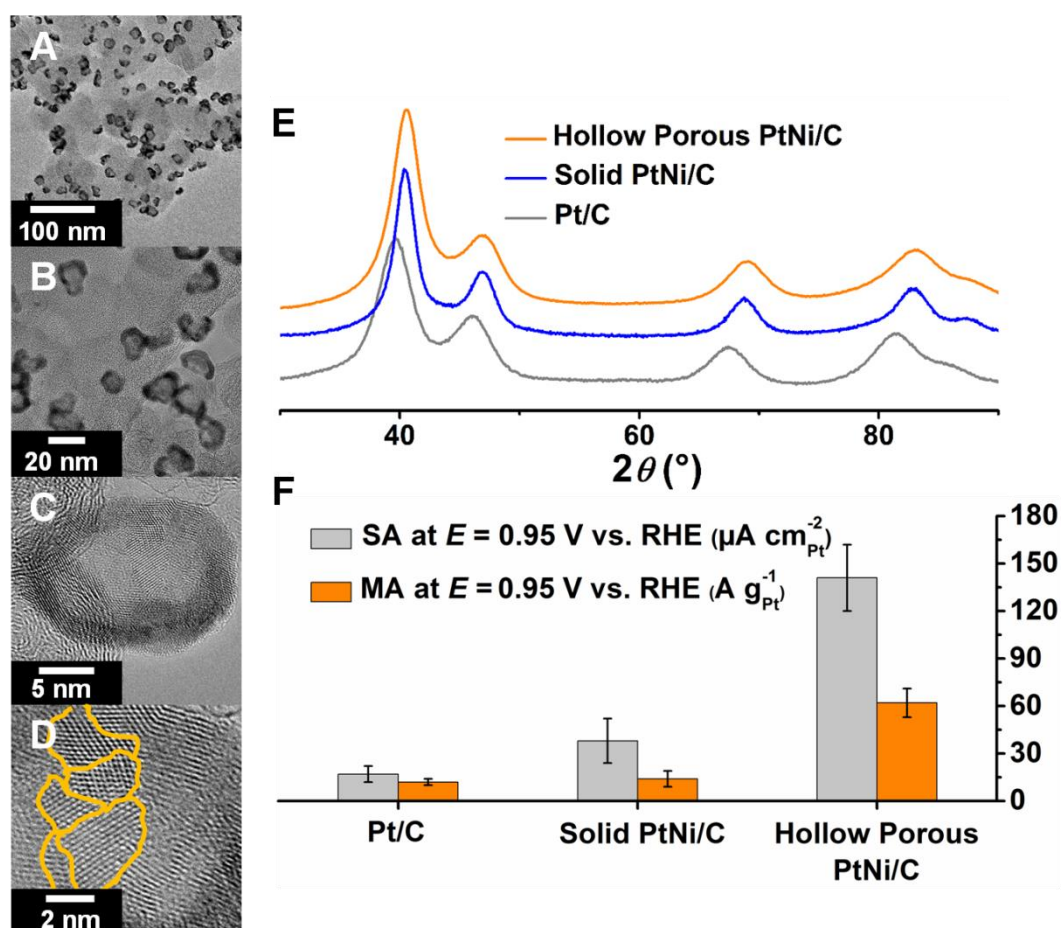


Figure 1. Structure – ORR activity relationships for PtNi/C electrocatalysts. (A-B) Low/medium magnification TEM images, and (C-D) HR-TEM images of porous hollow PtNi/C nanoparticles synthesized at room temperature. The boundaries between the individual nanocrystallites forming the PtNi shell in hollow nanoparticles are highlighted in orange (E) X-ray diffraction patterns measured on the hollow PtNi/C nanoparticles synthesized at room temperature, solid PtNi/C nanoparticles synthesized via a modified polyol route and on the commercial reference Pt/C electrocatalyst (provided by E-

TEK). (F) Specific and mass activity for the ORR measured at $E = 0.95$ V vs. RHE by Dubau *et al.* [28] Potential sweep rate $v = 0.005$ V s⁻¹, $\omega = 1600$ revolutions per minute (rpm), $T = 298 \pm 1$ K, 0.1 M HClO₄.

Figure 1A and 1B show that the hollow PtNi/C nanoparticles are polydisperse in size (average outer diameter 11.4 ± 1.9 nm are) and shape (spherical to ellipsoidal), and are homogeneously distributed on the Vulcan XC72 support. The high-resolution TEM image displayed in Figure 1C and 1D illustrate that the PtNi shell is constituted of individual crystallites (2-3 nm in size) with different crystallographic orientation and size, surrounding a central cavity. These nanocrystallites are interconnected by grain boundaries (highlighted in orange in Figure 1D). As recently shown by X-ray energy dispersive spectroscopy (X-EDS) elemental mapping in our former study, [28] the Pt and Ni atoms are homogeneously distributed within the metal shell. Note however that, due to acid leaching in the final step of the synthesis, the surface and subsurface layers of the hollow PtNi/C nanoparticles are enriched in Pt [27,28].

The X-ray diffraction (XRD) patterns measured on the hollow PtNi/C nanoparticles synthesized at room temperature, and on a commercial reference Pt/C electrocatalyst (provided by E-TEK) are shown in Figure 1E. For the sake of comparison, solid PtNi/C nanoparticles with similar crystallite size and chemical composition were synthesized via a modified polyol method (see Experimental Section), and used as an internal reference material. All the electrocatalysts featured a Pt mass fraction of 20 wt. %, and the Ni content was 16/21 at. % in the solid and porous hollow PtNi/C nanoparticles, respectively. Accordingly, the Pt lattice was contracted by 1.9 % in the hollow PtNi/C nanoparticles and by 1.7 % in the solid PtNi/C nanoparticles relative to Pt/C. These

values are commensurate with the Ni content, confirming the homogeneous distribution of Pt and Ni atoms in the PtNi/C electrocatalysts (Table 1).

Table 1. Chemical and structural parameters for the hollow PtNi/C electrocatalysts synthesized at various temperatures, the solid PtNi/C and the reference Pt/C electrocatalysts evaluated in this work.

	Atomic Composition ^a (% at.)	Lattice Parameter ^b (a, angstroms)	Lattice Contraction ^b (vs. Pt/C, %)
Pt/C	Pt ₁₀₀ Ni ₀	3.930	0
Solid PtNi/C	Pt _{84±1} Ni _{16±1}	3.864	1.7
Hollow PtNi/C - RT	Pt _{79±1} Ni _{21±1}	3.855	1.9
Hollow PtNi/C – 278 K	Pt _{80±3} Ni _{20±3}	3.851	2.0
Hollow PtNi/C – 293 K	Pt _{77±4} Ni _{23±4}	3.837	2.4
Hollow PtNi/C – 313 K	Pt _{86±0} Ni _{14±0}	3.870	1.5
Hollow PtNi/C – 333 K	Pt _{82±2} Ni _{18±2}	3.858	1.8
Hollow PtNi/C – 353 K	Pt _{81±2} Ni _{19±2}	3.865	1.7

^[a] The chemical composition was determined by atomic absorption spectrometry (AAS)

^[b] The lattice parameter (angstrom) and the lattice contraction vs. Pt/C (%) were determined by X-ray diffraction.

The degree of contraction of the Pt lattice influences the position of the *d*-band centre of Pt relative to the Fermi level, ^[10] and is thus a parameter of choice to rationalize the differences in ORR activity of various bimetallic electrocatalysts. It has been used by Dubau *et al.* ^[22–26] to build structure – ORR activity relationships for Pt₃Co/C nanoalloys

aged in real PEMFC devices. Using a similar approach, Jia *et al.* ^[21] constructed a Sabatier-volcano-type curve between the Pt-Pt distance (evaluated by extended X-ray absorption fine structure - EXAFS) and the ORR specific activity (measured in liquid electrolyte using a rotating disk electrode set-up) for various PtNi/C nanocatalysts before and after their operation in a real PEMFC device. However, it is clear that the degree of contraction of the Pt lattice fails in explaining the catalytic activity trends displayed in Figure 1F. Indeed, the slight lattice mismatch between the solid and the hollow PtNi/C electrocatalysts cannot explain the differences in ORR specific activity: $38 \pm 14 \mu\text{A cm}^{-2}_{\text{Pt}}$ and $141 \pm 21 \mu\text{A cm}^{-2}_{\text{Pt}}$ at $E = 0.95 \text{ V vs RHE}$ for the solid and the hollow PtNi/C nanoparticles, respectively ^[28].

In an effort to rationalize these differences, a set of hollow PtNi/C electrocatalysts with different Ni content, Pt lattice parameter and crystallite size was composed by controlling and varying the temperature at which the synthesis was performed (from 278 K to 353 K). Representative TEM images of the hollow PtNi/C nanoparticles synthesized at different temperatures, and the associated distribution of the external (d_{ext}) and internal (d_{in}) diameters are displayed in Figure 2. In general, increasing the temperature of the synthesis resulted in increased diameter of the central void (d_{in}) and the PtNi shell thickness ($e_{\text{shell}} = (d_{\text{ext}} - d_{\text{in}})/2$). This is precisely quantified in Table 2, Figure S1 and Figure S2 where the average values of d_{ext} , d_{in} and e_{shell} are shown. Since the masses of Pt and Ni salt precursors were kept identical for all syntheses, the results suggest that a lower density of sacrificial Ni-rich/C nanoparticles and thus thicker Pt-rich shells were formed at elevated synthesis temperatures.

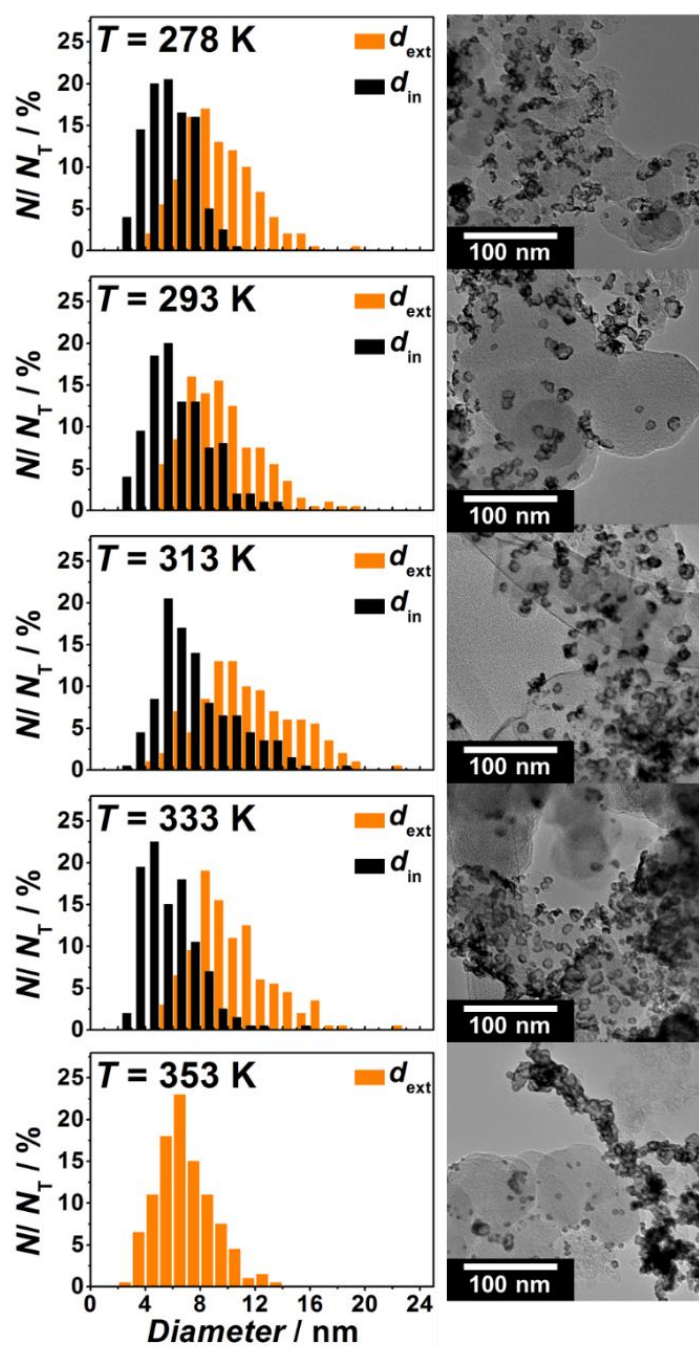


Figure 2. Representative TEM images and particle size distributions of PtNi/C electrocatalysts synthesized at various temperatures. The external diameter (d_{ext}) was measured on isolated PtNi/C nanoparticles only. The large degree of agglomeration of the PtNi/C catalyst synthesized at $T = 353$ K prevented the determination of the internal diameter (d_{in} , *i.e.* the diameter of the central cavity).

Table 2. Morphological characteristics of the electrocatalysts evaluated in this work (commercial Pt/C, solid PtNi/C and hollow PtNi/C nanoparticles synthesized at various temperatures).

	External diameter ^a (d_{ext} , nm)	Inner diameter ^a (d_{in} , nm)	Shell thickness ^a (e_{shell} , nm)	Average crystallite size (d_{XRD} , nm)
Pt/C	2.7 ± 0.9	-	-	2.2
Solid PtNi/C	2.2 ± 0.7	-	-	2.9
Hollow PtNi/C - RT	12.8 ± 2.3	7.6 ± 2.1	2.6 ± 0.7	2.4
Hollow PtNi/C – 278 K	9.4 ± 2.6	5.6 ± 1.7	1.9 ± 1.1	1.9
Hollow PtNi/C – 293 K	9.7 ± 2.8	6.3 ± 2.3	1.7 ± 1.3	2.0
Hollow PtNi/C – 313 K	11.5 ± 3.5	7.6 ± 2.8	1.9 ± 1.6	2.8
Hollow PtNi/C – 333 K	10.3 ± 2.9	5.7 ± 2.0	2.3 ± 1.2	2.8
Hollow PtNi/C – 353 K	6.8 ± 2.0	b	b	2.8

^[a] The external and internal diameter and the shell thickness (nm) were determined from the statistical analyses of TEM images

^[b] The large degree of agglomeration of the PtNi/C catalyst synthesized at $T = 353$ K prevented any determination of the internal diameter (d_{in} , *i.e.* the diameter of the central cavity). The external diameter (d_{ext}) was measured on isolated PtNi/C nanoparticles only.

We rationalized the decreased density of sacrificial Ni-rich/C nanoparticles with increasing temperature based on the half-life time of sodium borohydride (NaBH_4) used as a reducing agent. Indeed, according to Mochalov *et al.* ^[35] and Minkina *et al.*, ^[36]

BH_4^- ions hydrolyse slowly at low temperature (their half-life time are high), thereby increasing the reducing power of the NaBH_4 solution. Conversely, when the synthesis is performed at high temperature, the BH_4^- ions decompose rapidly and decrease the reducing power of the NaBH_4 solution. The greater stability of BH_4^- at low temperature favours the nucleation of Ni-rich/C nanoparticles on the Vulcan XC72 support, and results into thinner PtNi shells. *A contrario*, the fast hydrolysis of BH_4^- at high temperature limits the number of nuclei being generated on the Vulcan XC72 support, therefore resulting into thicker PtNi shells and eventually collapsing and aggregation of PtNi/C nanoparticles as can be seen in Figure 2 (this holds especially true for the catalyst synthesized at 353 K). We also noticed that the morphological characteristics of the hollow PtNi/C nanoparticles synthesized at room temperature (*i.e.* without temperature control, $T = 298 \pm 5$ K) resemble those of hollow PtNi/C nanoparticles synthesized at $T = 313$ K or $T = 333$ K. However, such discrepancy is not surprising because the hydrolysis of BH_4^- ions is exothermic and causes an increase of the temperature of the synthesis solution if the latter is not thermostated.

The changes in structure in turn impacted the specific surface area of the hollow PtNi/C nanoparticles. The experimentally measured Pt specific surface area (determined using CO_{ads} stripping coulometry, $S_{\text{Pt,CO}}$) reached $55 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$ for the hollow PtNi/C nanoparticles synthesized at $T = 278$ K and decreased to $40 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$ for those synthesized at $T = 313$ K. Based on the large diameters of the hollow PtNi/C nanoparticles, the high Pt specific surface area may appear surprising but can easily be rationalized by considering porosity in the hollow PtNi/C nanoparticles. To gain fundamental insights on the possibility for molecules to access the inner surface, a comparison between the experimentally measured ($S_{\text{Pt, CO}}$) and the theoretical Pt specific surface area was

achieved. The theoretical Pt specific surface area was estimated using the model described by Montejano-Carrizales *et al.*,^[37,38] assuming that the hollow PtNi/C nanoparticles display a cubooctahedral shape and that the CO:Pt stoichiometry equals 1. Two cases were considered: the external surface ($S_{\text{ext, theo}}$) only or both the internal and the external surfaces ($S_{\text{ext, theo}} + S_{\text{in, theo}}$) are electrochemically active. Figure 3 unambiguously shows that the second scenario gives the best agreement *i.e.* that the hollow PtNi/C nanoparticles are highly porous.

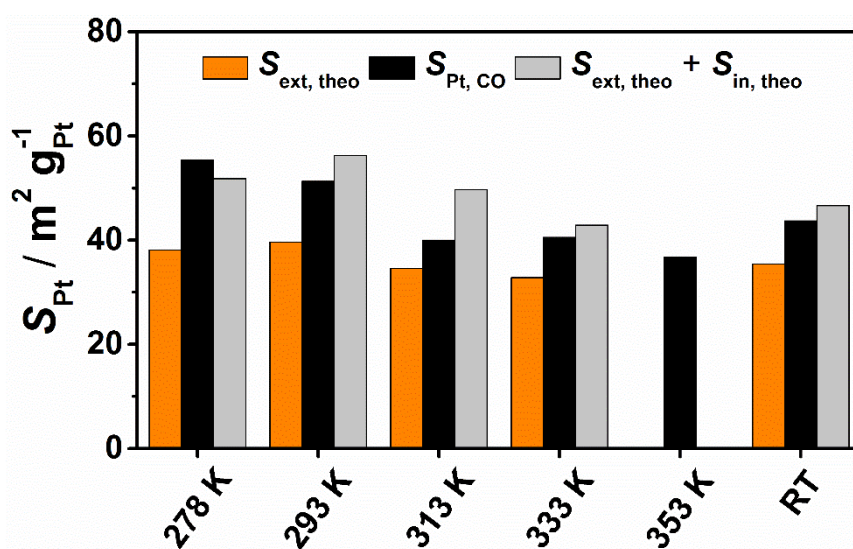


Figure 3. Theoretical and measured Pt specific surface areas for the hollow PtNi/C electrocatalysts synthesized at various temperatures. The experimental Pt specific surface area was calculated by CO_{ads} stripping ($S_{\text{Pt, CO}}$), and compared to the theoretical specific surface area determined assuming that the porous hollow PtNi/C nanoparticles display an ideal cubooctahedral shape and a CO:Pt stoichiometry equal to 1. Two cases were considered: (i) CO molecules adsorb only on the external surface ($S_{\text{ext, theo}}$) or (ii) CO molecules adsorb on the external and the internal surfaces of the PtNi/C nanoparticles ($S_{\text{ext, theo}} + S_{\text{in, theo}}$). Due to its dual morphology (solid and hollow PtNi/C agglomerates), the comparison could not be performed on the PtNi/C electrocatalyst synthesized at $T = 353 \text{ K}$.

Figure 4 displays electrochemical characteristics and ORR activity of the porous hollow PtNi/C electrocatalysts synthesized at different temperatures.

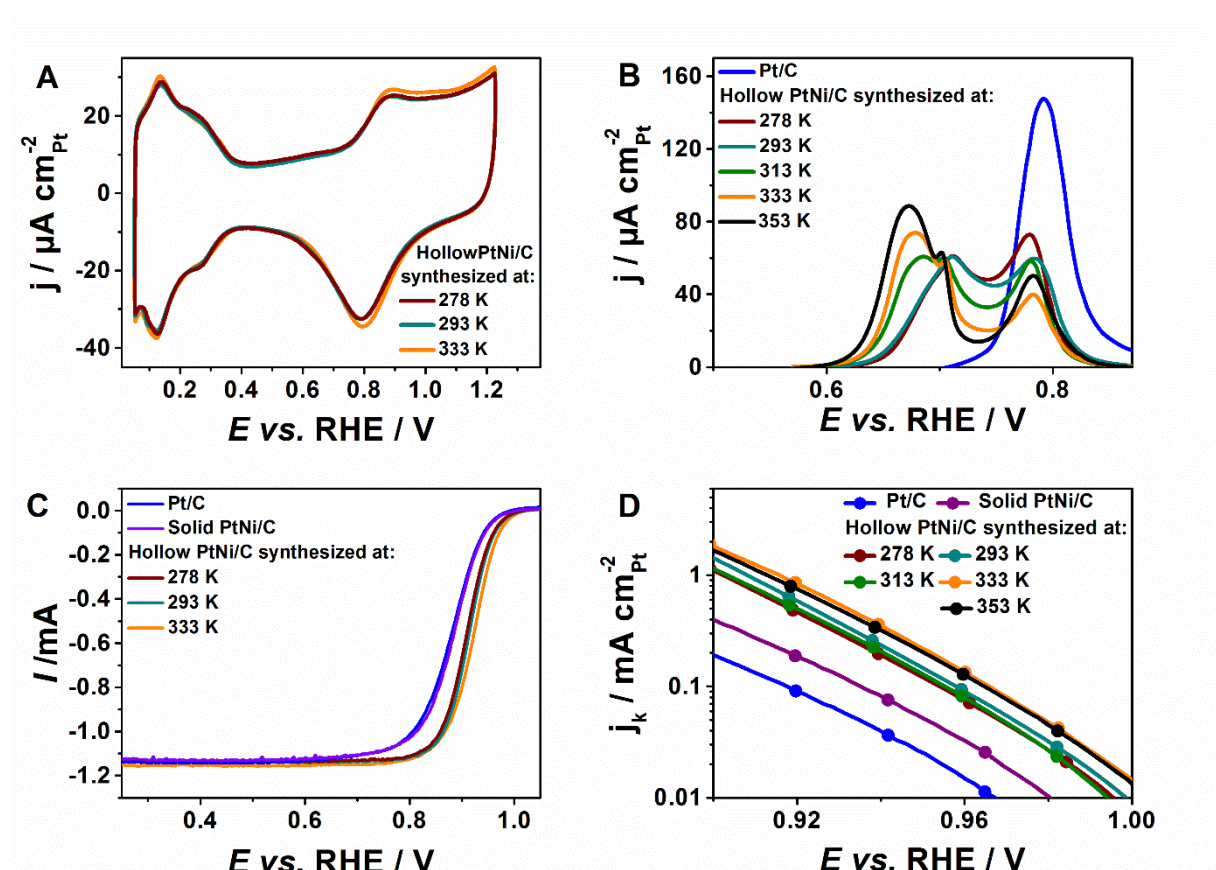


Figure 4. Electrochemical study on the electrocatalysts evaluated in this work.

(A) Base voltammograms for porous hollow PtNi/C electrocatalysts synthesized at $T = 278 \text{ K}$, $T = 293 \text{ K}$ or $T = 333 \text{ K}$ in Ar-saturated 0.1 M HClO_4 – $\nu = 20 \text{ mV s}^{-1}$; (B) CO_{ads} stripping voltammograms measured on the electrocatalysts synthesized at different temperatures and on the reference Pt/C in 0.1 M HClO_4 . $\nu = 20 \text{ mV s}^{-1}$; (C) Positive-going ORR voltammograms recorded in O_2 -saturated 0.1 M HClO_4 on the solid PtNi/C electrocatalyst, on the porous hollow PtNi/C electrocatalysts synthesized at $T = 278 \text{ K}$, $T = 293 \text{ K}$ or $T = 333 \text{ K}$, and on the reference Pt/C catalyst ($\nu = 5 \text{ mV s}^{-1}$, $\omega = 1600 \text{ rpm}$); (D) Tafel plot of the mass-transport corrected kinetic current obtained in O_2 -sat-

urated 0.1 M HClO₄ at $v = 5 \text{ mV s}^{-1}$, $\omega = 1600 \text{ rpm}$ for the PtNi/C electrocatalysts synthesized at different temperatures and the Pt/C reference. Other conditions: $T = 298 \pm 1 \text{ K}$, Pt loading = $20 \mu\text{g cm}^{-2}$.

The nearly superimposed base cyclic voltammograms (CVs) displayed in Figure 4A suggest that the Pt:Ni ratio and the elemental distribution in the surface and near-surface layers are independent on the synthesis temperature for hollow PtNi/C electrocatalysts. We related this to the highly corrugated ‘Pt-skeleton’ nanostructure resulting from the last step of the synthesis (a 22 h treatment in 1 M H₂SO₄, see Experimental Section). As shown by Durst *et al.* [39] on Pt₃Co/C nanoparticles, this treatment causes removal of Co atoms from the second and third atomic layers and formation of a Pt-rich surface with under-coordinated atoms. Since Ni and Co atoms have similar standard potential, atomic radius and interdiffusion coefficient, the same phenomena are believed at work here.

On the contrary, the CO_{ads} stripping measurements revealed very sensitive to the temperature at which the hollow PtNi/C nanoparticles were synthesized. The CO_{ads} stripping voltammograms featured a pre-peak comprised between $0.60 < E < 0.73 \text{ V vs. RHE}$ and a main peak located at $E = 0.78 - 0.79 \text{ V vs. RHE}$ (Figure 4B). The presence of multiple CO_{ads} stripping voltammograms on bimetallic nanoparticles is classically rationalized by considering four effects in the literature: (i) the ligand effect, (ii) the bifunctional effect [40–42], (iii) a preferential crystallographic orientation of the nanoparticles or (iv) the presence of grain boundaries between the metal nanocrystallites [30–32,43]. In the frame of the ligand effect, the addition of Ni to Pt would weaken the interaction between the catalytic surface and adsorbed CO molecules, thereby resulting in

a decreased CO_{ads} coverage. In the frame of the bi-functional mechanism, Ni atoms would adsorb and dissociate H₂O molecules at lower electrode potentials relative to pure Pt sites, thereby providing more facile oxidation of CO_{ads} molecules adsorbed on neighbouring Pt sites. However, based on the small variations of the Ni content in the catalysts (Table 1), and the fact that all catalytic surfaces are Pt-rich (they were acid-leached in the last step of the synthesis, see Experimental Section), these two effects are highly unlikely to account for the observed differences in CO_{ads} stripping voltammograms. To justify that the crystallographic orientation of the bimetallic nanoparticles is playing a minor role in CO_{ads} stripping voltammograms, we refer to the work of Ahmadi *et al.* [44,45]. The authors [45] showed that the position of the CO_{ads} stripping peak in acidic electrolyte neither depends on the Pt:Ni ratio in the surface and near-surface region nor on the crystallographic orientation of the surface, suggesting that strain and ligand effect are dominating over ensemble effect (preferential crystallographic orientation of the nanoparticles).

Hence, we conclude that the presence of multiple peaks in the CO_{ads} electrooxidation voltammograms is related to their fine nanostructure, in particular to the presence of structural defects such as grain boundaries. The presence of grain boundaries in the PtNi shell is not surprising if one considers the large difference lattice mismatch between Pt and Ni atoms (close to 10 %). Such mismatch favours Volmer-Weber type growth that is the formation of Pt-rich clusters onto the Ni-rich/C nanoparticles rather than complete Pt monolayers. As the reduction of Pt²⁺ ions originally in solution proceeds, these clusters transform into Pt-rich nanocrystallites which grow and ultimately contact each other via grain boundaries. Similar three-dimensional growth mode was

reported by Price *et al.* [47] for Pd²⁺ onto Au cores using EXAFS measurements. Evidences of 3D growth may also be found in the HR-TEM pictures of hollow PtNi/C nanocrystallites displayed in Figure 5, where grain boundaries *i.e.* frontiers between the different PtNi crystallites have been highlighted in orange.

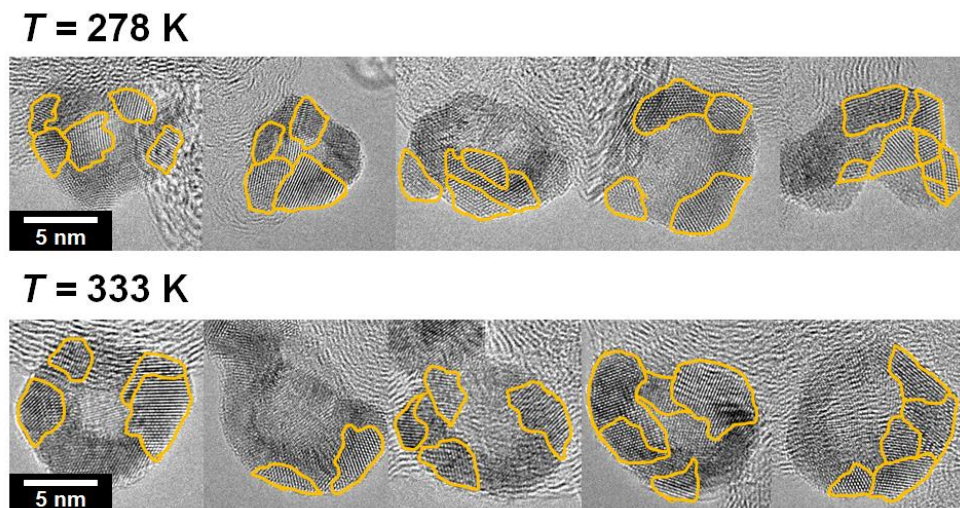


Figure 5. HR-TEM images of porous hollow PtNi/C nanoparticles synthesized at $T = 278$ K and $T = 333$ K. The boundaries between the individual PtNi nanocrystallites are highlighted in orange.

Note however that no quantitative determination of the volumic density of grain boundaries could be achieved since the HR-TEM images are 2D projections of 3D nanoparticles, and since the observed grain boundaries can indifferently be due to nanocrystallites that are in the zone axis or to adjacent nanocrystallites. An interesting observation was that the PtNi lattice is strongly distorted in the neighbourhood of adjacent nanocrystallites. Similar findings were made by Wang *et al.* on NiAl nanocrystallites [48]. This strong distortion of the PtNi lattice prohibited any clear indexation of the crystallographic facets in presence. However, for the same reasons than those mentioned before, it could hardly be distinguished on how many atomic rows the distortion extends, and if it relaxes linearly or abruptly for example via dislocations.

Other defects such as voids and pores are also clearly visible in Figure 5. These bulk defects are a consequence of the nanoscale Kirkendall effect, a vacancy-activated interdiffusion mechanism in bimetallic alloys, where one of the elements interdiffuses faster than the other. In the case of hollow PtNi/C nanoparticles, the fast interdiffusion of Ni atoms during the deposition of Pt^{2+} ions from solution acts a strong driving force for an inwards flux of vacancies. Once present in the nanoparticle, these vacancies grow and ultimately collapse in the centre. In summary, we argue that the ‘pre-peak’ located in CO_{ads} stripping voltammograms is a fingerprint of planar (grain boundaries) and bulk defects (cavity, voids) present in the hollow PtNi/C nanoparticles.

We now focus our attention to the electrocatalytic activity for the ORR of the different PtNi/C electrocatalysts. Thin film rotating disk electrode polarization curves recorded in O_2 -saturated 0.1 M HClO_4 are shown in Figure 4C. The corresponding Tafel plots corrected from Ohmic drop and diffusion in solution are represented in Figure 4D, and the specific activity and the mass activity for the ORR at $E = 0.95$ V vs. RHE ($\text{SA}_{0.95}$ and $\text{MA}_{0.95}$, respectively) extracted from the Tafel plots are listed in Table 3 (and plotted in Figure S3). For the sake of comparison with other studies, the specific and the mass activity for the ORR were also calculated at $E = 0.9$ V vs. RHE ($\text{SA}_{0.90}$ and $\text{MA}_{0.90}$, respectively) and are displayed in Table S1 and Figure S4.

Table 3. ORR activity measured at $E = 0.95$ V vs. RHE and specific surface area ($S_{\text{Pt,co}}$) for the porous hollow PtNi/C synthesized at various temperatures, and the reference solid PtNi/C and Pt/C electrocatalysts.

	Specific activity ^[a] ($\mu\text{A cm}^{-2}_{\text{Pt}}$)	Mass activity ^[a] ($\text{A g}^{-1}_{\text{Pt}}$)	Specific surface area ^[a] ($\text{m}^2 \text{g}^{-1}_{\text{Pt}}$)
Pt/C	26 ± 3	21 ± 2	83 ± 7
Solid PtNi/C	70 ± 20	26 ± 5	42 ± 6
Hollow PtNi/C - RT	157 ± 16	66 ± 7	43 ± 4
Hollow PtNi/C – 278 K	109 ± 12	60 ± 11	56 ± 8
Hollow PtNi/C – 293 K	126 ± 17	62 ± 10	51 ± 7
Hollow PtNi/C – 313 K	129 ± 25	53 ± 6	42 ± 5
Hollow PtNi/C – 333 K	190 ± 30	77 ± 15	41 ± 3
Hollow PtNi/C – 353 K	170 ± 35	62 ± 13	37 ± 2

^[a]The ORR curves were recorded in O_2 -saturated 0.1 M HClO_4 at $T = 298 \pm 1$ K using a potential sweep rate $\nu = 0.005$ V s^{-1} and $\omega = 1600$ rpm. The specific activity ($\mu\text{A cm}^{-2}_{\text{Pt}}$) and the mass activity ($\text{A g}^{-1}_{\text{Pt}}$) for the ORR were corrected from the Ohmic losses and from diffusion in solution. Pt loading: $20 \mu\text{g cm}^{-2}$. Each data point is the average of at least three independent experiments. The specific surface area was determined from CO_{ads} stripping voltammograms assuming $420 \mu\text{C cm}^{-2}_{\text{Pt}}$.

We first notice a 1.75-fold enhancement in ORR specific activity at $E = 0.95$ V vs RHE between the best (synthesis performed at $T = 333$ K) and the worst (synthesis performed at $T = 278$ K) porous hollow PtNi/C electrocatalysts. Concomitantly, the Tafel slopes remained in the order of $50 \text{ mV decade}^{-1}$ in the kinetic region ($0.90 < E < 0.96$

V vs. RHE). To better understand these differences in ORR activity, the specific activity of the porous hollow PtNi/C nanoparticles was plotted as a function of the Pt lattice contraction relative to Pt/C, the Ni content determined by AAS, the average crystallite size calculated from X-ray diffraction patterns ((111), (100) and (110) orientations (d_{XRD})), and the texture coefficient ($\text{TC}(\text{hkl})$), *i.e.* the susceptibility for PtNi crystallites to be preferentially oriented. As can be seen in Figure 6, the parameters which are usually used to rationalize the specific activity for the ORR of bimetallic nanocatalysts namely the strain, ligand and the ensemble effects [6,9,20] showed no direct correlation with the ORR activity trends.

The highest ORR specific activity was observed for the electrocatalyst synthesized at $T = 333$ K, which features a Ni content close to 18 at. % (Figure 6B) and a 1.8 % contraction of the Pt lattice relative to pure Pt/C (Figure 6A). This result agrees with the recent findings of Jia *et al.* [21] on solid and porous PtNi/C nanoparticles using EXAFS as a mean to estimate the Pt-Pt distance. Similar trends for the degree of contraction of the Pt lattice (Figure 6A) and the Ni content (Figure 6B) confirmed that the Pt-Pt distance is commensurate with the atomic composition. However, two electrocatalysts (synthesized at $T = 278$ K and $T = 353$ K) were systematically out of the trend reported in Figure 6A and Figure 6B, thereby showing that other parameters play a role in the enhancement of the ORR activity. For example, because of its peculiar morphology (mixture of highly agglomerated solid and hollow PtNi/C nanoparticles), the electrocatalyst synthesized at $T = 353$ K featured a lower lattice strain than expected based on its Ni content but was one of the best performing. On the contrary, despite a nearly-optimal Pt lattice contraction, the electrocatalyst synthesized at $T = 278$ K was performing nearly two times less than the catalyst synthesized at $T = 333$ K.

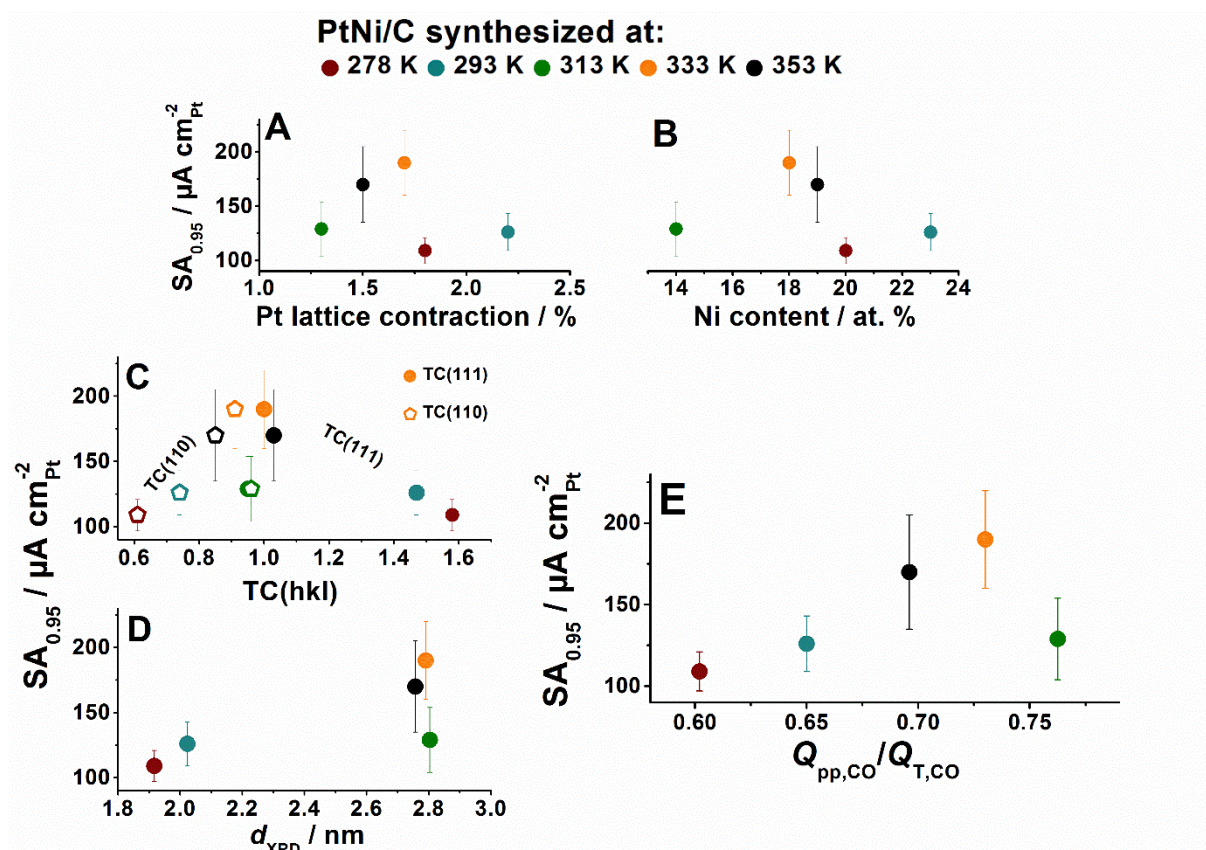


Figure 6. Structure – catalytic activity relationships for the porous hollow PtNi/C nanoparticles synthesized at various temperatures. The specific activity for the ORR measured at $E = 0.95$ V vs. RHE and corrected from Ohmic losses and diffusion in solution is plotted vs. (A) the degree of contraction of the Pt lattice vs. Pt/C (B) the Ni at. % determined by AAS, (C) the texture coefficient (TC(hkl)) for the (111) (TC(111)) and the (110) crystallographic orientations (TC(110)) vs. a commercial Pt/C catalyst, (D) the average crystallite size of the porous hollow PtNi/C electrocatalysts (d_{XRD}) determined from the X-ray diffraction peaks from (111), (110) and (100) planes using Scherrer's law or (A) the ratio of the electrical charge of the CO_{ads} stripping pre-peak ($Q_{pp,CO}$) to the total CO_{ads} stripping charge ($Q_{T,CO}$).

Table 4 probes an eventual influence of the crystallographic orientation of the porous hollow PtNi/C nanoparticles on the ORR kinetics.

Table 4. Structural properties of the porous hollow PtNi/C nanoparticles synthesized at various temperatures. Using the X-ray diffraction patterns from the (111), (100) and (110) crystallographic orientations, the texture coefficient (TC(hkl)) and the crystallite sizes of the porous hollow PtNi/C nanoparticles were calculated.

(hkl)	Texture coefficient ^[a] (TC, dimensionless)			Crystallite size ^[a] (d_{XRD} / nm)			
	(111)	(100)	(110)	(111)	(100)	(110)	Average
Hollow PtNi/C – 278 K	1.58	0.92	0.61	1.84	1.82	2.09	1.92
Hollow PtNi/C – 293 K	1.47	1.03	0.74	2.03	1.85	2.19	2.02
Hollow PtNi/C – 313 K	0.95	1.18	0.94	3.28	2.40	2.73	2.80
Hollow PtNi/C – 333 K	1.00	1.08	0.91	3.23	2.32	2.82	2.79
Hollow PtNi/C – 353 K	1.03	1.20	0.85	3.23	2.35	2.69	2.76

^[a] The texture coefficient (TC(hkl)) and the crystallite size of the porous hollow PtNi/C nanoparticles were calculated using the X-ray diffraction patterns from the (111), (100) and (110) crystallographic orientations.

The texture coefficients (TC) of the synthesized electrocatalysts were calculated according to the formula introduced by Ciapina *et al.* ^[49] (see. Materials and Methods). TC(hkl) values greater than 1 signify that a preferential orientation exists along the (hkl) plane. Conversely, TC(hkl) values smaller than 1 indicate that the (hkl) plane is underrepresented relative to the reference Pt/C material. Figure 6C and Figure S5 show that the best performing PtNi/C electrocatalyst features the lowest TC(111) (slightly larger than 1), the highest TC(110) and a moderate TC(100) coefficient. Although we

have no insight on the crystallographic orientation of the facets exposed to O₂ molecules, we notice that texture also cannot account for the observed catalytic trends (the ORR specific activity varies as (100) < (110) ~ (111) on Pt single crystals ^[50] in HClO₄).

In agreement with the literature on Pt/C ^[51,52] or PtCo/C nanoparticles ^[53], the specific activity for the ORR of the porous hollow PtNi/C electrocatalysts increased with an increase of the crystallite size (Figure 6D). Many reasons have been invoked for the crystallite size effect, but their discussion is beyond the scope of this article (the interested reader is referred to dedicated review articles ^[51,54]). One exception to the linear relationship plotted in Figure 6D is for the electrocatalyst synthesized at $T = 313$ K. The small Ni content of this catalyst (14 at. %, see Figure 6B) and the resulting small Pt lattice contraction (Figure 6A) as well as the high density of defects on its surface (Figure 6E) are believed to account for its poor ORR performance.

Last, we discovered a clear and unequivocal relationship between the ratio of the charge under the CO_{ads} electrooxidation pre-peak ($Q_{pp, CO}$, *i.e.* the grain boundaries) to the total CO_{ads} electrooxidation charge ($Q_{T, CO}$) and the specific activity for the ORR (Figure 6E). At first sight, this relationship may appear counterintuitive since the appearance of the CO_{ads} electrooxidation pre-peak results from a preferential adsorption of OH species, which are active species for the electrochemical CO_{ads} oxidation but poisoning species for the ORR (they limit the number of catalytic sites available for O₂ dissociation and charge transfer). In order to better understand the observed catalytic trends, we refer to data published for stepped single crystal surfaces. According to Hitotsuyanagi *et al.* ^[55] and Kuzume *et al.*, ^[56] the specific activity for the ORR is optimal for $n = 5$ on stepped Pt[$n(111) \times (100)$] single crystal surfaces and for $n = 3$ on stepped

Pt[$n(111) \times (111)$], respectively. Since Pt(111) surfaces feature the closest to optimal OH binding energy ^[7] and since steps strongly bind oxygenated species (OH_{ads} and O_{ads}), this relationship is surprising. However, it was recently rationalized by Bandarenka *et al.* ^[57] who showed that the OH binding energy on (111) terraces is weakened when the step density is increased, thereby resulting in a volcano-curve between the step density and the ORR specific activity. The authors suggested that a decreased solvation of the adsorbed hydroxyl intermediates on adjacent terrace sites is responsible for the volcano-type curve. Similarly to what was proposed by Bandarenka *et al.* ^[57], we hypothesize that structural defects present on the nanoparticles surface, such as grain boundaries, may function as highly active sites for water dissociation leading to interrupted network of co-adsorbed oxygenated species and water molecules, weaker binding of oxygenated species on the neighbouring catalytic sites and thus faster ORR kinetics.

Another possible explanation is that grain boundaries and, more generally structural defects, are highly active sites for the ORR. Indeed, it is well-documented that grain boundaries display less dense atomic arrangement and distorted lattice relative to individual nanocrystallites ^[58]. As recently shown by Calle-Vallejo *et al.* ^[59] on a Pt(111) surface, these characteristics may offer catalytic sites with enhanced ORR activity. A precise quantification of the impact of grain boundaries on ORR activity enhancement is currently undergoing in our group using high-resolution transmission electron microscopy and Synchrotron X-ray diffraction. Preliminary results revealed that PtNi/C samples featuring high microstrain values (inhomogeneous Pt-Pt distance) are highly active for the ORR, thereby confirming the results presented in this study.

Last, we emphasize that much smaller $Q_{pp, CO}/Q_{T, CO}$ ratios were measured for the reference solid Pt/C and PtNi/C nanomaterials (e.g. 0 for the solid Pt/C and 0.24 for the solid PtNi/C) compared to those found for porous hollow PtNi/C nanoparticles. We believe that these values confirm the points developed in this paper. Indeed, as discussed previously, the effect of grain boundaries adds to the strain and ligand effects *i.e.* the ORR catalytic enhancement for the ORR will be different depending on the type and volumic density of grain boundaries present in the nanomaterials. In this respect, since the size of the nanoparticles is nearly equivalent to that of the constituting crystallites in the reference PtNi/C sample (Table 2), there is no or little grain boundaries except those formed by agglomeration of nanoparticles and thus it is not surprising that this catalysts is less efficient than the hollow PtNi/C nanoparticles. Similarly, as the reference Pt/C catalyst is composed of solid isolated Pt/C nanoparticles and does not contain Ni atoms, there is no strain / ligand /structural effect contributing to its ORR activity.

Conclusion

In summary, we synthesized and characterized a set of porous hollow PtNi/C electrocatalysts with different physico-chemical properties (Ni content, lattice parameter, specific surface area). No relationship could be established between the specific activity for the ORR measured at $E = 0.95$ V vs. RHE and the Pt lattice contraction relative to Pt/C or the Ni content of the porous hollow PtNi/C nanoparticles. On the contrary, we established a clear relationship between the ratio of the electrical charge of the CO_{ads} stripping pre-peak ($Q_{pp, CO}$) to the total CO_{ads} stripping charge ($Q_{T, CO}$), which is a structural marker of the concentration of structural defects (such as grain boundaries) and the specific activity for the ORR measured at $E = 0.95$ V vs. RHE. The present study

highlights that, in addition to well-known strain, ligand and ensemble effects, the density of structural defects on the electrocatalysts surface contributes to the enhancement of the ORR activity.

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Experimental section

Reference Electrocatalysts

A Pt/Vulcan XC72 catalyst with a weight fraction (wt. %) of 20 % was purchased from E-TEK, and used as reference material without any treatment. The number-averaged Pt nanoparticle size was 2.9 ± 0.6 nm. A solid PtNi/C catalyst was prepared using a modified polyol method. Calculated amounts of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99.9 %) and NiCl_2 (Alfa Aesar Puratonic, 99.9995 %) were first dissolved in a 20 mL vial of deionized water and ethylene glycol (EG, EG:water volume ratio 1:1). Meanwhile, the appropriate amount of Vulcan XC72 was dispersed by sonication in a separate 20 mL vial of 1:1 EG:water mixture. The content of each vial was then mixed in 20 mL of pure EG. The pH of the obtained mixture was adjusted to 10 using a 0.5 M NaOH solution (diluted in 1:1 EG:water mixture). The suspension was kept under continuous

stirring while (i) being refluxed at $T = 433$ K for $t = 3$ h under argon and (ii) cooled down at room temperature under air for $t = 12$ h. The pH was then adjusted to 3 using a 0.5 M H_2SO_4 aqueous solution, and the solution was allowed to stand for $t = 24$ h. The solution was finally filtered and washed with deionized water before being dried at $T = 383$ K for 1 h.

Synthesis of Porous Hollow PtNi/C Electrocatalysts

A determined number of moles of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ (Alfa Aesar Premion 99.995 % metal basis) and of NiCl_2 (Alfa Aesar Anhydrous 99.99 % metal basis) were first dissolved in 150 mL of deionized water with 0.3 g of dispersed Vulcan XC72 (Cabot) targeting 20 wt. % Pt weight fraction. An aqueous solution of sodium borohydride (Aldrich 99.99 %, 208 mg dissolved in 25 mL) was added at a 5 mL min^{-1} rate, while the solution was kept under magnetic stirring at $T = 278$ K, $T = 293$ K, $T = 313$ K, $T = 333$ K, $T = 353$ K or at room temperature ($T = 298 \pm 5$ K). After $t = 1$ h, the solution was filtered, washed by Milli-Q water and dried for $t = 45$ min at $T = 383$ K. The resulting powder was then acid treated, under magnetic stirring, in a 1 M H_2SO_4 solution – $T = 298 \pm 5$ K – during $t = 22$ h.

X-ray Diffraction Measurements

The X-ray diffraction patterns of the catalysts were determined using a PANalytical X'Pert Pro MPD vertical goniometer / diffractometer with a diffracted-beam monochromator ($\text{Cu K}\alpha$ radiation wavelength $\lambda = 0.15406$ nm) operating at 45 kV and 40 mA. The 2θ range was 10° to 125° and a step size 0.033° . The crystallite size following (111), (100) and (110) directions was obtained from the FWHM (full width at half max-

imum) of the (111), (100) and (110) diffraction peaks, using the Debye-Scherrer equation. The texture coefficient (T_c) of the $(hkl)_i$ plane was determined using the following equation:

$$T_c(hkl)_i = \frac{I(hkl)_i}{I_0(hkl)_i} \bigg/ \frac{1}{N} \sum_{i=1}^n \frac{I(hkl)_i}{I_0(hkl)_i} \quad [2]$$

Where $I(hkl)_i$ stands for the surface of the $(hkl)_i$ peak, $I_0(hkl)_i$ stands for the surface of the $(hkl)_i$ peak for the reference catalyst (here a commercial 20 wt. % Pt/C from E-TEK) and N was the total number of planes taken in consideration (4 in this study, *i.e.* (111), (200), (220) and (311)).

Transmission Electron Microscopy

The particle size distribution was determined from the TEM images obtained at low/medium magnification (x 150 000) on a JEOL 2010 TEM operating at 200 kV with a point-to-point resolution of 0.19 nm. Considering the irregular shape of the nanoparticles, the internal and external Feret diameters were calculated to establish the particle size distribution while, for the commercial catalyst (20 wt. % Pt/C from E-TEK), the number averaged diameter was determined for the particle size distribution, *i.e.*:

$$\overline{d_N} = \frac{\sum_{i=1}^n l_i d_i}{\sum_{i=1}^n l_i} \quad [3]$$

l_i stands for the number of nanoparticles having a diameter d_i . The shell thickness of the porous hollow PtNi/C nanoparticles was determined as half of the difference between the external and internal Feret diameters. High resolution transmission electron

microscopy (HR-TEM) images of the porous hollow PtNi/C nanoparticles synthesized at room temperature were acquired using a JEM-ARM 200F (JEOL) microscope equipped with a cold-field emission gun and an image aberration corrector operated at an accelerating voltage of 200 kV.

Atomic Absorption Spectrometry

The Ni and Pt content of each electrocatalyst was established by AAS (PinAAcle 900F, Perkin Elmer). 5 +/- 1 mg of the electrocatalyst was first digested in aqua regia (3:1 HCl: HNO₃ by volume) made from high purity acid (37 vol. % ACS Reagent Sigma Aldrich; 65 vol. % Sigma Aldrich) during 72h at T = 298 +/- 1 K. The solution was then diluted 7 times to reach the AAS range for Pt and Ni. The Ni and Pt content were then determined as a comparison of three series of three measurements. The Pt-related wavelength was $\lambda = 266$ nm and the Ni-related one $\lambda = 232$ nm.

Electrochemical Measurements in Liquid Electrolyte.

All the glassware accessories used in this study were (i) cleaned by soaking overnight in a H₂SO₄ + H₂O₂ mixture, (ii) thoroughly washed with Milli-Q water, (iii) boiled in Milli-Q water and (iv) washed with fresh electrolyte solution (0.1 M HClO₄) prior to any experiment. The electrochemical measurements were performed using an Autolab PGSTAT302N in a four-electrode electrochemical cell thermostated at T = 298 K. The electrolyte solution was daily prepared with Milli-Q water (Millipore, 18.2 M Ω) and HClO₄ 96 wt. % (70% Merck Suprapur). The reference electrode was a commercial reversible hydrogen electrode (RHE, Hydroflex, Gaskatel GmbH) connected to the cell via a Luggin capillary. The counter electrode was a glassy carbon plate connected to the potentiostat by a gold wire. A platinum wire was connected to the reference to filter

the high frequency noise and to avoid any low-frequency disturbance of the electrochemical measurements. The working electrodes were prepared by depositing 10 μL of a suspension (10 mg PtNi/C or Pt/C, 54 μL of Nafion 5 wt. % (Sigma Aldrich), 3600 μL of H_2O Milli-Q and 1446 μL of isopropyl alcohol (99.5 % Acros Organics), homogenized by sonication) on a glassy carbon disk (0.196 cm^2 , Sigradur). This aliquot was then dried at room temperature while rotating at 500 rpm. Prior to any electrochemical measurement, a fresh working electrode was immersed into the deaerated electrolyte at 0.1 V vs. RHE. The electrochemical experiments were then performed: (i) 50 cyclic voltammograms between 0.05 and 1.23 V vs. RHE at $\nu = 500 \text{ mV s}^{-1}$, (ii) 3 cyclic voltammograms between 0.05 and 1.23 V vs. RHE at $\nu = 20 \text{ mV s}^{-1}$ (iii) CO_{ads} stripping voltammograms to determine the electrochemically active surface area. We assumed that the electrooxidation of a CO_{ads} monolayer requires 420 μC per cm^{-2} of Pt. A full CO coverage was first established by bubbling CO for 6 min and purging with Ar for 29 min while keeping the electrode potential a 0.1 V vs. RHE. Then, 3 cyclic voltammograms were performed at 20 mV s^{-1} between 0.05 and 1.23 V vs. RHE; (iv) the ORR activity was measured in O_2 -saturated 0.1 M HClO_4 by linear sweep voltammetry at 5 mV s^{-1} from 0.20 to 1.05 V vs. RHE at different revolution rates (400, 900, 1600 and 2500 rpm). The ORR mass/specific activity was determined at $E = 0.95 \text{ V vs. RHE}$ after correction from the Ohmic drop and from the oxygen diffusion in solution.

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